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14. ABSTRACT After seminal work presented a decade ago, ionic liquids (IL) have now received a lot of attention as energetic materials for propellant applications. ^[1-3] In bipropellant rocket engines, it is desirable to achieve ignition by means of a hypergolic reaction and so to minimize system complexity. Hypergolic bipropellants are defined as fuel and oxidizer combinations that, upon contact, chemically react and release enough heat to spontaneously ignite, eliminating the need for an additional ignition source. This also makes them highly reliable for spacecraft and satellites which need to fire their rocket engines hundreds, or even thousands, of times during their lifetime. Unfortunately, no reliable <i>a priori</i> method for prediction of hypergolicity for fuel – oxidizer pairs is available today. The initial “hunting for the hypergol”, as John Clark entitled one of the chapters in his book <i>Ignition!</i> , took place mainly during WWII. ^[4] At that time, such toxic systems as “C-Stoff” (a mixture of N ₂ H ₄ ·H ₂ O, methanol and water) and others consisting of triethyl amine, aniline, toluidine, xyldine and N-methyl aniline were developed. Today, environmental and health concerns are becoming more and more pressing in the propellant world. Nevertheless, hydrazine and its methylated derivatives are still the state-of-the-art fuels for bipropellant applications. Most of the problems handling hydrazine and its derivatives are related to their volatility, as they are carcinogenic vapor toxins. For these reasons, it is exceedingly attractive to replace hydrazine with ILs which have become paragons of environmental friendliness, green chemistry and low vapor toxicity.					
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Ionic liquid hypergols!** (PREPRINT)

Tommy Hawkins, Michael Rosander, Ghanshyam Vaghjiani, Steven Chambreau, Gregory Drake and Stefan Schneider*

After seminal work presented a decade ago, ionic liquids (IL) have now received a lot of attention as energetic materials for propellant applications.^[1-3] In bipropellant rocket engines, it is desirable to achieve ignition by means of a hypergolic reaction and so to minimize system complexity. Hypergolic bipropellants are defined as fuel and oxidizer combinations that, upon contact, chemically react and release enough heat to spontaneously ignite, eliminating the need for an additional ignition source. This also makes them highly reliable for spacecraft and satellites which need to fire their rocket engines hundreds, or even thousands, of times during their lifetime. Unfortunately, no reliable *a priori* method for prediction of hypergolicity for fuel – oxidizer pairs is available today.

The initial “hunting for the hypergol”, as John Clark entitled one of the chapters in his book *Ignition!*, took place mainly during WWII.^[4] At that time, such toxic systems as “C-Stoff” (a mixture of N₂H₄·H₂O, methanol and water) and others consisting of triethyl amine, aniline, toluidine, xylydine and N-methyl aniline were developed. Today, environmental and health concerns are becoming more and more pressing in the propellant world. Nevertheless, hydrazine and its methylated derivatives are still the state-of-the-art fuels for bipropellant applications. Most of the problems handling hydrazine and its derivatives are related to their volatility, as they are carcinogenic vapor toxins. For these reasons, it is exceedingly attractive to replace hydrazine with ILs which have become paragons of environmental friendliness, green chemistry and low vapor toxicity.

Most of the focus in energetic ILs research has been on heterocyclic cations in combination with oxygenated anions which frequently have stability and safety problems.^[e.g. 5-7] In a bipropellant system, with ILs used as fuels, it is not necessary to use an oxygen balanced IL. Furthermore, one can avoid oxygen-carrying anions completely which, other things being equal should make handling much safer. In a salt system, the cation carries a positive charge and is therefore much more resistant towards oxidation. Consequently, fuel rich anions are much easier to oxidize and hold the potential to actually promote hypergolic ignition of the material.

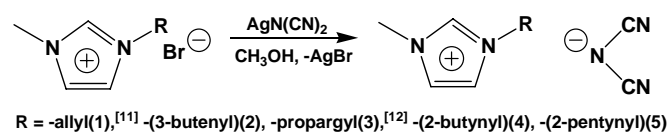
Disappointingly, our first ignition tests carried out with ILs containing fuel-rich azide anions did not reveal any hypergolic properties.^[8] However, the violent nature of the reactions was an encouragement to continue this line of work.

And so the aim of this paper is to report on investigations of the feasibility of other fuel rich anions, especially the dicyanamide anion, to promote IL hypergolicity.

Dicyanamide was chosen, not only because it is a fuel-rich anion, but, more importantly, because IL dicyanamides have some of the lowest viscosity among known ILs.^[9, 10] In bipropellant systems, pumps transport fuel and oxidizer and so, excessive viscosity must be avoided.

Imidazolium-based heterocyclic systems were first considered because they generally possess greater stability than their triazolium or tetrazolium analogues. Unsaturated sidechains, like allyl, propargyl and 2-butenyl were selected because it was hoped that they would initiate or promote hypergolic ignition. It has been demonstrated in the past that unsaturated, especially acetylenic, compounds show a tendency to hypergolicity and can even be used as fuel additives to promote hypergolic ignition.^[4]

The starting materials, 1-R-3-methylimidazolium bromides (**1-5**), were prepared by alkylation of methylimidazole followed by metathesis with freshly prepared silver dicyanamide (Scheme 1).



Scheme 1. Synthesis of 1-R-3-methylimidazolium dicyanamides (**1-5**).

Because silver dicyanamide is insoluble in methanol, it can be used in excess assuring complete conversion. Physical data for known **1**, **3** and novel compounds, **2**, **4**, **5**, are shown in Table 1 along with the 1-methyl-4-amino-1,2,4-triazolium analogue **6** which is discussed later and was prepared by the same method.

Table 1. Thermal and physical data of the dicyanamide salts 1-6.

1-R-3-methylimidazolium	T _g /°C ^[a]	T _m /°C ^[b]	T _d /°C ^[c]	η/cP ^[d] (25°C)
1-allyl-	-85		+207	42
1-(3-butenyl)-	-90		+210	27
1-propargyl-	-61	+17 ^[12]	+144	110
1-(2-butenyl)-		+49	+179	
1-(2-pentynyl)-		+59	+184	
1-methyl-4-amino-1,2,4-triazolium	-66		+143	92

[a] glass transition [b] melting point [c] decomp. onset [d] viscosity

Most substituted imidazolium dicyanamides are true room temperature liquids. Compounds **4** and **5** are solid at ambient conditions and **5** could be recrystallized from methanol layered with diethylether, which gave crystals suitable for a single crystal X-ray determination. The structure analysis revealed an extensive hydrogen-bond network involving the dicyanamide anion (Figure

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1).^[13] Like in other ILs, extensive hydrogen bonding is responsible for solidification.

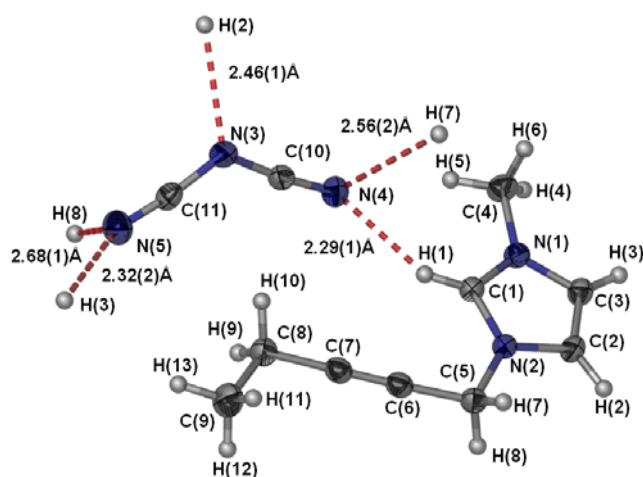


Figure 1. ORTEP diagram showing connectivity, conformation and the atom numbering scheme for **5**.

Ignition of propellants often constitutes a major hurdle in propellant development. Therefore, discovering an IL which shows hypergolic ignition with common oxidizers represents a major achievement. Compounds **1-3** are in fact the first ILs demonstrated to be hypergolic.

Droplet tests were carried out using a glass cuvette which was filled with 1ml of inhibited, red-fuming nitric acid (IRFNA: ~83% HNO_3 + 14% N_2O_4 + ~2% H_2O + 0.6% HF) or white fuming nitric acid (WFNA ~100% HNO_3). A syringe generating ca. 10 μL droplets was used to dispense the IL fuel (Figure 2a). A high speed camera recording 500frames/s was used to determine the ignition delay times (ID) (Table 2) by counting the frames between the droplet first hitting the surface of the oxidizer (Figure 2b) and sign of the first visible ignition (Figure 2c).

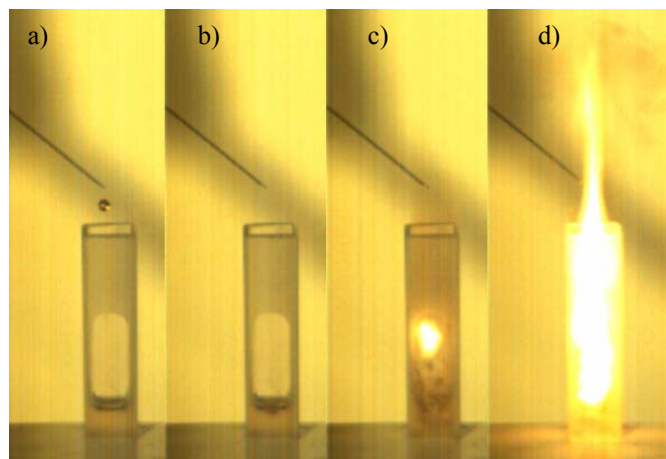


Figure 2(a-d). Selected frames from high-speed video of the hypergolic reaction of **3** and WFNA.

After this discovery, one example of an IL based on a triazole, **6**, and three commercially available IL dicyanamides, 1-butyl-3-methyl-imidazolium, 1-butyl-1-methylpyrrolidinium and n-butyl-

3-methyl-pyridinium were tested and found to be hypergolic as well (Table 2).

Unexpectedly, unsaturated substituents do not seem to play a determinative role in the ignition process. These results suggest that the key to these hypergolic ILs may be found within the dicyanamide anion. For a suitable hydrazine replacement, ID times of less than 5ms are preferred. Aerosol-type fuel and oxidizer sprays are being examined and should lead to shorter ID times as well as reflecting real-world engine conditions.

Table 2. ID times for hypergolic ILs with IRFNA and WFNA.

1-R- 3-methylimidazolium dicyanamide	IRFNA ID [ms]	WFNA ID [ms]
1-allyl-	625	43
1-(3-butenyl)-	670	n.d. ^[a]
1-propargyl-	170	15
1-methyl-4-amino- 1,2,4-triazolium	n.d.	31
1-butyl ^[b]	n.d.	47
1-butyl-1-methyl- pyrrolidinium ^[b]	n.d.	44
n-butyl-	n.d.	37
3-methylpyridinium ^[b]		

[a] n.d.=not determined [b] purchased from Merck

With the discovery of these IL hypergols, a new path for transitioning these materials into bipropellant applications seems clear. It is expected that these systems can now be fine tuned for energy content, performance, and desirable physical properties and that they can replace and surpass state-of-the-art, highly toxic hydrazine and its derivatives.

Experimental Section

Methanol (99.93% A.C.S. HPLC grade, Aldrich), diethyl ether (anhydrous, 99+%, A.C.S. Reagent, Aldrich), $\text{NaN}(\text{CN})_2$ (Degussa) and AgNO_3 (Strem Chemicals) were used as received. The substituted imidazolium bromides^[14] and 1-methyl-4-amino-1,2,4-triazolium iodide,^[15] and $\text{AgN}(\text{CN})_2$ ^[9] were prepared according to literature procedures. Nonvolatile solids and liquids were handled in the dry nitrogen atmosphere of a glove box. Raman spectra (500mW, 25°C) were recorded in the range 4000-80 cm^{-1} on a Bruker Equinox 55 FT-RA 106/S spectrometer using a Nd-Yag laser at 1064 nm. 5mm glass NMR tubes were used as sample containers. Nuclear magnetic resonance spectra were recorded on a Bruker Spectrospin DRX 400 MHz Ultrashield™ spectrometer at room temperature with each salt sample being measured as a neat liquid or dissolved in $\text{DMSO}-d_6$ in 5mm NMR tubes. The ^1H , ^{13}C spectra were referenced to external samples of neat TMS; ^{15}N spectra of neat liquids were referenced to external samples of neat nitromethane. Melting points were determined by differential scanning calorimetry using a Thermal Analyst 200, Dupont 910 Differential Scanning Calorimeter. Measurements were carried out at a heating rate of 10°C/min in sealed aluminum pans with a nitrogen flow rate of 20mL/min. The reference sample was an empty Al container which was sealed in the nitrogen atmosphere of a glove box. Viscosities were measured using a Brookfield RVDV-II+Pro viscometer equipped with a CPE-40 cone spindle at 10RPM connected to a Brookfield TC-502 temperature controller set at 25°C.

General procedure for preparation of salts (1-6). To a 100mL Schlenk flask equipped with a Teflon stir bar and purged with nitrogen the 1-R-3-methyl-imidazolium bromides (or 1-methyl-4-amino-1,2,4-triazolium iodide) were added and dissolved in ca. 30mL of methanol. In the dark a ca. 5% excess of freshly prepared silver dicyanamide was added to the stirred solution. Stirring was continued overnight.

The insoluble silver halide and excess silver dicyanamide were removed by filtration. The solvent was removed under reduced pressure yielding the desired ionic liquid dicyanamides.

1-allyl-3-methyl-imidazolium dicyanamide (1). 14.0 g (69.3 mmol) 1-allyl-3-methyl-imidazolium bromide was used for the metathesis. Yield 94%; red liquid; Raman (cm^{-1}) $\nu = 3159(9)$, 3090(16), 3023(27), 2988(26), 2957(41), 2886(10), 2828(8), 2192(100), 2135(10), 1646(27), 1565(8), 1448(10), 1414(26), 1386(8), 1338(11), 1293(15), 1218(6), 1108(7), 1042(6), 1022(25), 953(7), 918(7), 904(8), 762(9), 666(16), 623(9), 568(7), 499(7), 395(8), 314(7), 267(9), 182(51), 95(70), 84(71); δ_{H} (neat liquid) 9.01(1H, s), 7.49(1H, t, J 1.6), 7.48(1H, t, J 1.6), 5.81-5.71(1H, m, CH_2CHCH_2), 5.09-5.05(2H, m, CH_2CHCH_2), 4.69(2H, d, CH_2CHCH_2 , J_{H} 1.0), 3.71(3H, s, CH_3); δ_{C} 136.5, 131.2, 123.7, 122.2, 120.1, 119.1, 51.1, 36.3; δ_{N} -201.7, -210.6, -216.5, -369.9.

1-(3-butenyl)-3-methyl-imidazolium dicyanamide (2). 1.8 g (8.3 mmol) 1-(3-butenyl)-3-methyl-imidazolium bromide was used for the metathesis. Yield 93%; amber liquid; Raman (cm^{-1}) $\nu = 3162(6)$, 3083(12), 3005(25), 2982(21), 2959(38), 2921(21), 2869(6), 2831(5), 2196(63), 2137(5), 1642(23), 1566(5), 1459(6), 1418(26), 1387(10), 1340(13), 1299(9), 1235(3), 1210(2), 1169(1), 1111(3), 1022(19), 932(3), 906(4), 843(3), 745(0+), 703(2), 664(9), 623(1), 601(8), 540(0+), 417(3), 339(1), 270(4), 181(31), 84(100); δ_{H} (neat liquid) 9.92(1H s), 8.50(1H, s, br), 8.43(1H, s, br), 6.57-6.47(1H, m $\text{CH}_2\text{CH}_2\text{CHCH}_2$), 5.81-5.73(2H, m, $\text{CH}_2\text{CH}_2\text{CHCH}_2$), 5.09(2H, t, J_{H} 6.8 $\text{CH}_2\text{CH}_2\text{CHCH}_2$), 4.69(3H, s, CH_3), 3.36(2H, d, J_{H} 6.7 $\text{CH}_2\text{CH}_2\text{CHCH}_2$); δ_{C} 138.0, 134.9, 125.0, 123.9, 120.7, 120.2, 50.2, 37.8, 35.4; δ_{N} -198.8, -209.6, -216.5, -368.2.

1-propargyl-3-methyl-imidazolium dicyanamide (3). 5.8 g (28.8 mmol) 1-(3-butenyl)-3-methyl-imidazolium bromide was used for the metathesis. Yield 86%; dark red liquid; Raman (cm^{-1}) $\nu = 3162(5)$, 3108(6), 3013(4), 2958(24), 2942(21), 2876(2), 2826(3), 2193(100), 2130(48), 1571(4), 1414(19), 1387(9), 1342(7), 1284(2), 1211(1), 1163(2), 1106(5), 1021(17), 963(4), 904(3), 870(1), 744(2), 667(14), 614(6), 541(0+), 489(0+), 457(5), 399(4), 312(12), 272(9), 184(40), 96(56); δ_{H} (DMSO- d_6) 9.22(1H s), 7.79(1H, t, J_{H} 1.8), 7.75(1H, t, J_{H} 1.8Hz), 5.20(2H, d, J 2.6 CH_2CCH), 3.88(3H, s, CH_3), 3.84(1H, t, J_{H} 2.6 CH_2CCH); δ_{C} 137.0, 124.5, 122.6, 119.5, 79.4, 76.6, 38.9, 36.4.

1-(2-butenyl)-3-methyl-imidazolium dicyanamide (4). 1.1 g (5.3 mmol) 1-(2-butenyl)-3-methyl-imidazolium bromide was used for the metathesis. Yield 97%; amber solid; Raman (cm^{-1}) $\nu = 3157(6)$, 3108(8), 3071(6), 2958(35), 2936(30), 2926(48), 2850(6), 2744(1), 2317(4), 2240(29), 2195(100), 2136(7), 1573(4), 1448(7), 1428(15), 1411(20), 1383(10), 1335(8), 1314(2), 1262(1), 1249(1), 1168(2), 1120(3), 1021(19), 983(0+), 908(3), 790(0+), 746(4), 665(13), 635(8), 617(2), 454(6), 405(9), 364(12), 323(3), 265(3), 187(41), 85(54); δ_{H} (DMSO- d_6) 9.19(1H s), 7.76(1H, s, br), 7.71(1H, s, br), 5.11(2H, q, J_{H} 2.1 CH_2CCCH_3), 3.88(3H, s, CH_3), 1.90(3H, t, J_{H} 2.1 CH_2CCCH_3); δ_{C} 136.8, 124.4, 122.5, 119.5, 85.0, 71.8, 39.5, 36.3, 3.6.

1-(2-pentynyl)-3-methyl-imidazolium dicyanamide (5). 1.3 g (5.7 mmol) 1-(2-pentynyl)-3-methyl-imidazolium bromide was used for the metathesis. Yield 79% (after recrystallization from methanol solution layered with diethyl ether); dark brown solid; Raman (cm^{-1}) $\nu = 3157(4)$, 3095(11), 3063(7), 2974(16), 2958(28), 2936(47), 2924(38), 2883(14), 2848(8), 2725(1), 2311(4), 2241(29), 2198(100), 2136(12), 1574(2), 1444(10), 1428(22), 1411(17), 1385(6), 1339(8), 1321(12), 1261(4), 1169(2), 1118(2), 1090(2), 1062(6), 1021(19), 963(4), 906(4), 745(3), 664(10), 634(8), 614(2), 512(4), 440(3), 396(5), 363(5), 269(8), 245(7), 184(35), 86(59); δ_{H} (DMSO- d_6) 9.25(1H s), 7.79(1H, t, J_{H} 1.6), 7.75(1H, t, J_{H} 1.6), 5.16(2H, t, J_{H} 2.1 $\text{CH}_2\text{CCCH}_2\text{CH}_3$), 3.89(3H, s, CH_3), 2.31-2.26(2H, m, $\text{CH}_2\text{CCCH}_2\text{CH}_3$) 1.09(3H, t, J_{H} 7.5 $\text{CH}_2\text{CCCH}_2\text{CH}_3$); δ_{C} 136.8, 124.4, 122.5, 119.5, 90.2, 72.1, 39.4, 36.4, 13.7, 12.1.

1-methyl-4-amino-1,2,4-triazolium dicyanamide (6). 0.7 g (3.3 mmol) 1-methyl-4-amino-1,2,4-triazolium iodide was used for the metathesis. Yield 89%; colorless liquid; Raman (cm^{-1}) $\nu = 3156(4)$, 3034(3), 2960(13), 2814(2), 2736(0+), 2237(3), 2197(100), 2136(8), 1632(1), 1571(3), 1537(1), 1407(19), 1327(1), 1216(1), 1174(2), 1089(9), 1074(8), 1045(1), 981(8), 907(4), 738(3), 664(10), 617(9),

543(0+), 455(4), 312(3), 187(35), 85(64); δ_{H} (neat liquid) 10.67 (1H, s), 9.74 (1H, s), 7.39 (2H, s, NH_2), 5.00(3H, s, CH_3); δ_{C} 146.2, 144.0, 120.1, 40.4; δ_{N} -86.3, -169.3, -189.5, -305.4(t, $^1J_{\text{H}}$ 72), -218.5, -368.2.

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- [1] T.W. Hawkins, A. Brand, M. Petrie, D. Bach, M. McKay, Proceedings of the High Energy Density Matter, Contractors Conference, 1-3 June in Chantilly, VA, PL-TR-97-3057 **1997**.
- [2] M. Freemantle, *Chem. Eng. News*, **2007**, 85, 23-26.
- [3] J.M. Shreeve, R.P. Singh, R.D. Verma, D.T. Meshri, *Angew. Chem.*, **2006**, 118, 3664-3682; *Angew. Chem. Int. Ed.*, **2006**, 45, 3584-3601.
- [4] J.D. Clark, *Ignition!*, Rutgers University Press, New Brunswick, New Jersey, **1972**.
- [5] C.B. Jones, R. Haiges, T. Schroer, K.O. Christe, *Angew. Chem.*, **2006**, 118, 5303-5308; *Angew. Chem. Int. Ed.*, **2006**, 45, 4981-4984.
- [6] T. Hawkins, L. Hall, K. Tollison, A. Brand, M. McKay, *Propellants, Explos., Pyrotech.*, **2006**, 31, 196-204.
- [7] J.C. Gálvez-Ruiz, G. Holl, K. Karaghiosoff, T.M. Klapötke, K. Löhnitz, P. Mayer, H. Nöth, K. Polborn, C.J. Rohbogner, M. Suter, J.J. Weigand, *Inorg. Chem.*, **2005**, 44, 4237-4253.
- [8] S. Schneider, T. Hawkins, M. Rosander, J. Mills, R.D. Rogers, D.M. Drab, M. Smiglak, *submitted for publication*.
- [9] Y. Yoshida, K. Muroi, A. Otsuka, G. Saito, M. Takahashi, T. Yoko, *Inorg. Chem.*, **2004**, 43, 1458-1462.
- [10] D.R. MacFarlane, J. Golding, S. Forsyth, M. Forsyth, G.B. Deacon, *Chem. Commun.*, **2001**, 1430-1431.
- [11] G. Laus, G. Bentivoglio, H. Schottenberger, V. Kahlenberg, H. Kopacka, H. Roeder, T. Roeder, H. Sixta, *Lenzinger Ber.*, **2005**, 84, 71-85.
- [12] Y. Gao, H. Gao, C. Piekarski, J.M. Shreeve, *Eur. J. Inorg. Chem.*, **2007**, .
- [13] Crystal data for $\text{C}_{11}\text{H}_{13}\text{N}_5$: $M_r=215.26$, triclinic, space group $P-1$, $a=8.564(2)$, $b=8.731(2)$, $c=9.149(2)\text{\AA}$, $\alpha=107.85(3)$, $\beta=99.40(3)$, $\gamma=111.59(3)^\circ$, $V=575.3(3)\text{\AA}^3$, $F(000)=228$, $\rho_{\text{calc}}=1.243\text{ g cm}^{-3}$, $Z=2$, $\mu=0.081\text{ mm}^{-1}$, crystal size $0.74 \times 0.27 \times 0.06\text{ mm}^3$, θ range 2.46 to 28.21, index ranges $-11 \leq h \leq 11$, $-11 \leq k \leq 11$, $-12 \leq l \leq 12$, $\text{MoK}\alpha$ ($\lambda=0.71073\text{\AA}$), $T=173(2)\text{ K}$, 6739 measured data (Bruker 3-circle, SMART APEX CCD with χ axis fixed at 54.748° , using the SMART V 5.625 program, Bruker AXS: Madison, WI, 2001), of which 2666 ($R_{\text{int}}=0.0199$) unique. Lorentz and polarization correction (SAINT V 6.22 program, Bruker AXS: Madison, WI, 2001), absorption correction (SADABS program, Bruker AXS: Madison, WI, 2001), transmission factors min/max ratio 0.803. Structure solution by direct methods (SHELXTL 5.10, Bruker AXS: Madison, WI, 2000), full-matrix least-squares refinement on F^2 , data/parameters ratio 14.0:1, final R indices [$I \geq 2\sigma(I)$]: $R1=0.0368$, $wR2=0.1021$, R indices (all data): $R1=0.0410$, $wR2=0.0976$, GOF on $F^2=1.028$. CCDC-xxxxxx contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_request/cif.
- [14] S. Schneider, G. Drake, L. Hall, T. Hawkins, M. Rosander, Z. *Anorg. Allg. Chem.*, **2007**, 633, 1701-1707.
- [15] G. Drake, T. Hawkins, K. Tollison, L. Hall, A. Vij, S. Sobaski, *ACS Symposium Series*, **2005**, 902, 259-302.

Hypergols

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Ionic liquid hypergols!



The hunt for an ionic liquid hypergol!

Ionic liquids possessing hypergolic properties with the commonly used oxidizers, IRFNA and WFNA have been discovered. The combination of heterocyclic cations and fuel-rich dicyanamide anions made this breakthrough possible.